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REPORT DOCUMENTATION PAGE

1a. REPT NA		1b. RESTRICTIVE MARKINGS NA	
2a. SEC NA		3. DISTRIBUTION / AVAILABILITY OF REPORT Distribution Unlimited; Approved for Public Release	
2b. DEC NA		5. MONITORING ORGANIZATION REPORT NUMBER(S) NA	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) INDU/DC/GMH/TR-83-31		7a. NAME OF MONITORING ORGANIZATION ONR	
6a. NAME OF PERFORMING ORGANIZATION Indiana University	6b. OFFICE SYMBOL (if applicable) NA	7b. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, VA 22217	
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry Bloomington, IN 47405		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract N00014-86-K-0366	
8a. NAME OF FUNDING / SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (if applicable)	10. SOURCE OF FUNDING NUMBERS	
8c. ADDRESS (City, State, and ZIP Code)		PROGRAM ELEMENT NO.	PROJECT NO.
		TASK NO.	R&T Code
		4134006	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Evaluation of a Supercritical Fluid Chromatograph Coupled to a Surface-Wave-Sustained Microwave-Induced Plasma Detector			
12. PERSONAL AUTHOR(S) Debra R. Luffer, Leonard J. Galante, Paul A. David, Milos Novotny, and Gary M. Hieftje			
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM TO	14. DATE OF REPORT (Year, Month, Day) July 11, 1988	15. PAGE COUNT 27
16. SUPPLEMENTARY NOTATION Accepted for publication in Analytical Chemistry			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
		Supercritical Fluid Chromatography, Spectroscopic Detector, Speciation, Nonmetal Detection, Sulfur Analysis, DTIC	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) A capillary supercritical fluid chromatograph was coupled to a surface-wave-sustained microwave-induced plasma (MIP) sustained with a surfatron. The chromatographic system, interface, and plasma source are described. The plasma was optimized for sulfur emission at 921.3 nm and used to detect a mixture of sulfur-containing polycyclics that had been separated by SFC. The linear dynamic range for these compounds is 3 orders of magnitude with detection limits of 25 pg/sec of sulfur for thiophene. The relative standard deviations for repetitive injections are typically 1 to 5% at concentrations well above the detection limit.			
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED//UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Distribution Unlimited	
22a. NAME OF RESPONSIBLE INDIVIDUAL Gary M. Hieftje		22b. TELEPHONE (Include Area Code) (812) 335-2189	22c. OFFICE SYMBOL E

OFFICE OF NAVAL RESEARCH

Contract N14-86-K-0366

R&T Code 4134006

TECHNICAL REPORT NO. 31

EVALUATION OF A SUPERCRITICAL FLUID CHROMATOGRAPH COUPLED TO
A SURFACE-WAVE-SUSTAINED MICROWAVE-INDUCED PLASMA DETECTOR

by

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Accepted for Publication

in

ANALYTICAL CHEMISTRY

Indiana University
Department of Chemistry
Bloomington, Indiana 47405

11 July 1988

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DTIC TAB	<input type="checkbox"/>
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INTRODUCTION

Capillary supercritical fluid chromatography (SFC) has been recognized as the separation method of choice for compounds that are not easily amenable to either gas or liquid chromatographic analysis (1-3). The former is ultimately limited by the involatility of large compounds or thermal lability at the high temperatures required in gas chromatography (GC). The latter suffers from a lack of element-selective detection methods (4) due to solvent interferences. A supercritical fluid mobile phase has been able to overcome some of these limitations because it can operate optimally at significantly lower temperatures than GC, its viscosity and solute diffusivities are between liquid and gaseous phases, and its solvating power approaches that of a liquid (5). In addition, the column effluent at atmospheric pressure is compatible with many GC detectors which offer sensitive and selective detection. It is for this reason that many detection schemes are being borrowed from GC and adapted to SFC. Some examples of this include SFC/MS (6,7), SFC/FTIR (8), SFC/FID (9-11), as well as thermionic (12), dual flame photometric (13), and ion mobility (14).

Of the many varied detection methods for chromatography which have been investigated, those based on atomic spectroscopy have become increasingly attractive due to their inherent selectivity, freedom from interferences, and multielement detection capability (15). In particular, plasma detectors possess several characteristics which make them even more appealing than flame-based photometric systems: these include improved sensitivity, a wide dynamic range, and fewer spectral interferences. Most importantly, with respect to chromatographic analyses, the plasma detector will often tolerate co-elution from a column because it is virtually element-specific (15).

The microwave-induced plasma (MIP) (16,17) has been successfully employed

as an element-specific detector for GC (15,18-20). The surface-wave-sustained MIP (surfatron) is particularly attractive due to its stable, reproducibly long, small-diameter plasma (21). In addition, it is relatively inexpensive, easy to construct, and produces an annular plasma in helium (22) which is believed to make it less likely to be extinguished by the high mass flow of mobile phase. This type of plasma can operate under low pressure or atmospheric conditions with argon or helium as the support gas, typically at relatively low flow rates (<300 mL/min). The surfatron MIP operates efficiently with low powers (<200 W) and the tuning adjustments are simple, which enables it to be operated with zero reflected power under a variety of experimental conditions (23). The detection limits found for GC/surfatron MIP are competitive with other detectors but can be further improved by decreasing the diameter of the discharge tube and/or increasing the microwave power (23,24). Based on these findings, it seems reasonable that this detector could be coupled to SFC and thereby provide sensitive and selective detection. In addition, the use of a carbon or hydrogen wavelength channel promises universal detection as well.

This paper will discuss the coupling of chromatograph and detector with an emphasis on the difficulties in designing this type of interface. The optimization of the system will be outlined as well. A separation of model sulfur-containing polyaromatic compounds will be demonstrated. Sulfur was chosen because of its prevalence in systems of toxicological, environmental and biochemical interest. Spectroscopic detection was performed solely in the near-infrared region of the spectrum because the sulfur atom lines in the near-IR were found to be much more intense than the sulfur ion lines near 545 nm in the visible. In addition, the lines in the near-IR are free from severe spectral interferences from intense C_2 band emission in the visible (25).

EXPERIMENTAL

Instrumentation

A schematic diagram of the instrumentation employed in this study appears in Figure 1. The components of the system are described below.

Chromatographic Equipment. The mobile phase chosen for these studies was supercritical fluid grade^R carbon dioxide (Scott Specialty Gases; Plumsteadville, PA). The gas was pre-filtered through a column filled with silica and charcoal in an approximate 4:1 ratio prior to filling a Varian Series 4100 syringe pump (Varian Aerograph; Walnut Creek, CA), which has been modified for pressure ramping (26).

The fused-silica column used in these studies had an inner diameter of 50 μm and was 10 m long. Deactivation prior to coating was performed by dynamically coating the column with a solution of 5% polymethylhydrosilane (85 cs) (Petrarch Systems, Inc.; Bristol, PA) in pentane, then sealing the column and heating it for five hours at 300 °C. The column was subsequently statically coated with 0.2 μm of an SE-30 stationary phase and cross-linked three times with azo-t-butane.

The column was heated via a circulating water bath (Haake Buchler Instruments, Inc.; Saddle Brook, NJ) rather than with a conventional GC oven because of the sensitivity of the detector to temperature-induced variations in CO₂ flow. Each time the oven heating circuit switched on, a brief surge occurred in the flow of CO₂ through the column, which in turn resulted in a spike in the baseline. Substitution of the water bath alleviated this problem. The temperature of the water bath was maintained at 90 °C for most experiments.

Injectors were performed with an HPLC valve (Valco Instrument Co., Inc.;

Houston, TX) possessing a manually-actuated 60 nl injection rotor (Special Order Model RCI4W.06/.2). The head of the column was seated as close as possible to the injection rotor without touching it, in order to eliminate band-broadening at the injection point. All injections were splitless, which yielded high sensitivity when the injections were performed at low pressure (<1300 psi). A pre-column filter with a 0.5 μ m stainless-steel replaceable frit (Upchurch Scientific, Inc.; Oak Harbor, WA) was connected to the sample-inlet port of the injector in order to prevent particulates from being injected with the sample. The entire injection apparatus was held just outside the water bath, so all injections were made at room temperature.

The decompression required for detection at atmospheric pressure was accomplished with the integral restrictor described by Guthrie and Schwartz (27).

Interface. A schematic representation of the interface is shown in Figure 2. The plasma was sustained inside a 0.6 cm o.d. x 0.4 cm i.d. fused-silica tube (William A. Sales Ltd.; Wheeling, IL). The end of the column was joined to the plasma-discharge tube with a standard Swagelok 1/4-in. to 1/16-in. stainless steel reducing union in the following way: A section of fused-silica tubing (320 μ m i.d. x 2 cm long) was glued with household glue into a Vespel^R/15% Graphite ferrule (Alltech Associates, Inc./Applied Science Labs; Deerfield, IL) which was in turn glued into the 1/16-in. nut. This fused-silica tubing then served as a sleeve which serves to support the SFC column and center it within the discharge tube. A Teflon ferrule was used to seal the discharge tube between the union and its 1/4-in. nut. An additional quartz tube (3 mm i.d. x 8 cm long) was inserted into the discharge tube and served as a nozzle to direct the SFC effluent into the microwave plasma. The outer diameter of this tube was matched to the inner diameter of the discharge

tube to provide a tight fit, and Teflon tape was used to create a seal between the two. The other end of the nozzle was drawn in a flame and tapered to an approximate exit diameter of 150 μm . The restrictor was seated so it abutted the end of the quartz nozzle.

It is essential to heat the plasma gas (He) and focus the column effluent into the plasma with the quartz nozzle. Otherwise, column effluent "freezes" onto the tip of the restrictor because of the rapid decompression of the mobile phase. This condensation causes poor baseline stability and detector "spiking". Accordingly, the plasma gas was preheated by passing it through several meters of resistively heated stainless-steel tubing that was maintained at 300 °C.

The proximity of the restrictor to the plasma is important. The restrictor was placed just before the tip of the nozzle and centered symmetrically so the column effluent was swept efficiently into the center of the annular plasma. The tip of the nozzle was optimally positioned approximately 5 mm from the plasma to minimize detector dead volume and prevent the fusion of the restrictor by the plasma.

Microwave-Induced Plasma Detector. Microwave plasmas can be sustained in a variety of cavity structures (17). The surfatron device used for these studies was constructed of brass by our departmental machine shop and is similar to the design of Abdallah et al. (28). Details concerning the construction, operation, and tuning of our device are available elsewhere (22). A detailed description of the surfatron configuration for these studies is available in a companion publication (29).

The plasma was viewed axially (end-on). Emission was measured with an optical system designed specifically for the near-infrared spectral region. A glass lens (23.5-mm diam., 71-mm f.l.) imaged the center of the plasma onto

the entrance slit of the monochromator (model EU-700, 0.35-m f.l., GCA/McPherson Instruments; Acton, MA) with a magnification of 1.25. The grating was ruled at 600 grooves/mm and blazed at 1000 nm. The photomultiplier tube (model 7102, Hamamatsu Corp.; Middlesex, NJ) was biased at -1250 V with a high-voltage supply (model 1121A, EG & G Princeton Applied Research; Princeton, NJ) and mounted in a thermoelectrically cooled housing (models 7102/117 and TE104RF-002, Products for Research, Inc.; Danvers, MA); tap water was employed as the heat-exchange medium. The monochromator was equipped with a Heath scan driver (model EU-700-51, Heath Co.; Benton Harbor, MI). The slit width used for the chromatographic study was 100 μ m, which resulted in a spectral bandpass of 0.4 nm. The output current of the PMT was measured with a picoammeter (model 414S, Keithley Instruments, Inc.; Cleveland, OH), and received by a strip-chart recorder (model SR-204, Heath Co.). A 4-pole filter (locally constructed) was inserted between the picoammeter and recorder in order to remove high-frequency noise when chromatograms were recorded. The cut-off frequency was set at either 2 or 5 Hz, depending on the severity of the noise.

The plasma was sustained in high-purity grade helium (Air Products, Tamaqua, PA). Thiophene (Eastman Kodak, Co.; Rochester, NY), thianaphthene (Aldrich Chemical Company, Inc.; Milwaukee, WI), dibenzothiophene (Aldrich Chemical Company, Inc.) and 1,2-benzodiphenylene sulfide (Aldrich Chemical Company, Inc.) were chosen as model compounds. These compounds were diluted with dichloromethane (Mallinckrodt, Inc., Paris, KY).

Procedures

With the surfatron tuning adjustments set near their optimal positions (22), the plasma was initiated by touching the inside of the discharge tube with a length of tungsten wire. However, this method reduces the lifetime of

the discharge tube because deposits of WO_2 accumulate on the inside of the tube. Alternatively, the plasma can be ignited with a short burst from a Tesla coil with the tuning adjustments set in such a way that the reflected power is maximal. Immediately after ignition, the tuning adjustments are set to zero reflected power. Once the plasma has stabilized, the CO_2 mobile phase can be introduced without fear of extinguishing the plasma. Unfortunately, the CO_2 accelerates devitrification of the discharge tube, as evidenced by a milky-white film that formed on the inner surface of the discharge tube where the plasma is sustained. Typically, the discharge tube lasts for one week at an applied microwave power of 125 W.

RESULTS AND DISCUSSION

Optimal Plasma Conditions For Sulfur Determinations

Discharge-Tube Length and Position. Although the absolute length of the discharge tube was 10.5 cm, the crucial factor was the length of quartz tube that extended from the end of the surfatron body. A protruding length of 5 mm or less resulted in a bluish plasma while carbon dioxide was being introduced. A length of tubing greater than 5 mm past the brass face plate resulted in a bright green plasma, even though all other conditions remained the same. Moreover, under identical chromatographic and spectroscopic conditions, a five-fold increase in signal-to-noise ratio arose when the analyte was excited in a green plasma rather than a blue plasma. Hence, for all studies described below, the discharge tube protruded at least 10 mm beyond the brass face plate.

A possible explanation for this phenomenon involves the amount of air that is entrained into the plasma. Hubert and co-workers (23) have ascertained that the entrainment of air, evidenced by an increase in the band emission of N_2 , is a function of the length of quartz tube that extends past the face plate of their surfatron. Similarly, Koirtzmann (30) noted that the sensitivity of chlorine, and especially fluorine, is strongly decreased if the N_2 concentration in the plasma is greater than about 2%, probably because the excitation temperature of the plasma is lowered. Work is currently underway in our laboratory to identify the bands which are responsible for the severe color change of the plasma that occurs when the discharge-tube position is altered in the manner described above.

Applied Microwave Power. The effect of applied microwave power on sulfur emission intensity was studied under chromatographic conditions by

injecting thiophene (see Figure 3a). It can be seen that peak height is relatively constant and optimal between 115 and 135 W. Moreover, baseline noise worsened and discharge-tube devitrification was accelerated at powers greater than 135 W, regardless of the tuning adjustments. A similar study was performed using the solvent (dichloromethane) by monitoring Cl emission at 912.1 nm. Once again, the baseline noise was low and relatively constant; the plot of relative signal versus applied power is shown in Figure 3b. As with sulfur emission, the Cl signal is maximal and relatively constant between 120 and 140 W. Based on these findings, an applied power of 120 W was chosen and used in all subsequent chromatographic optimizations.

Helium Flow Rate. The effect of helium flow rate on sulfur emission intensity was investigated under chromatographic conditions. The peak-height response of thiophene, shown in Figure 4a, reveals a relatively constant and maximal signal for flow rates from 120 to 260 mL/min. A similar trend was observed for signal-to-background noise ratio since the baseline noise was relatively constant with flow rate. As before, these results were verified with the Cl line (Figure 4b) and indicate a relatively constant signal between 120 and 270 mL/min.

A He flow rate of 250 mL/min was chosen for all subsequent measurements because of a related study on the effect of helium flow rate on the appearance of the plasma in the presence of the CO₂ mobile phase. When the flow rate of helium is low (<250 mL/min), the plasma assumes a pink-purple color and the annulus is difficult to distinguish because of the diffuse nature of the plasma. In contrast, when the flow rate is high (> 250 mL/min), the plasma is bright green and the annulus is clearly in evidence. A possible explanation for this difference in appearance is that CO₂ is not efficiently swept into the plasma at low flow rates of helium. Moreover, because of its high density

as a supercritical fluid, the CO_2 does not diffuse rapidly into the annular region of the plasma, so neither the CO_2 , nor the analyte it carries, can be atomized or excited efficiently. This explanation accounts for the pinkish color of the plasma characteristic of a helium-only plasma. On the other hand, when the helium flow rate is sufficient to sweep CO_2 into the plasma, the bright-green color indicative of C_2 band emission at 512.9 nm results (29). A possible disadvantage associated with the choice of a higher flow rate is the decreased residence time of analyte in the plasma. In view of the already high mass flow rate of CO_2 (40 $\mu\text{L}/\text{min}$ or 130 $\mu\text{g}/\text{sec}$), this consideration can be neglected.

The surfatron plasma is capable of tolerating much higher mobile phase flow rates than other MIP systems before signal stability seriously deteriorates. The plasma was able to sustain itself with added gas flow rates approaching 18 mL/min (15% of the support gas (v/v)) (29). Because the typical flow rates from a packed column are significantly larger than from a capillary column, the integrity of the plasma may not be maintained; however, the robustness of the surfatron detector allows the possibility of an interface to a packed column SFC system.

Determination of Sulfur-Containing Compounds

Model Compound Separation. A mixture of four polyaromatic sulfur-containing compounds was prepared and injected; the resulting separation is shown in Figure 5. It should be noted that this separation was performed without using the optimal parameters described above. Although these particular molecules are somewhat small to be considered good candidates for SFC, the mixture serves as a good indication of the sensitivity and selectivity of the plasma detector. The negative deflection immediately prior to peak #1 (thiophene) in Figure 5 corresponds to the solvent elution. The

same mixture was run under similar chromatographic conditions with FID detection and the thiophene could not be separated from the solvent peak, indicating the importance of the selectivity offered by the microwave-plasma detector.

A very prominent feature of this chromatogram is the decreasing background that occurs during a pressure ramp. The increased mass flow rate of CO₂ that accompanies higher column pressures is believed to quench the plasma, and to perturb it sufficiently to cause a feedback of reflected power into the generator. The slope of the baseline was found to parallel the rate at which the reflected power rises; it appears that this progressive detuning of the plasma results in a steady decrease in the amount of forward power that is effectively coupled into the plasma. Consequently, it is not surprising that later eluting peaks in a pressure-programmed run would be less intense than peaks that elute before a significant amount of detuning has occurred (Figure 5).

Detection Limits. The detection limits for the first three compounds of the four-component mixture were determined under the optimal conditions of operation and are listed in Table I. The somewhat poorer detection limits for the higher molecular-weight compounds appears to be due principally to quenching of the plasma by the carbon dioxide mobile phase at the high pressures required to elute these compounds. This hypothesis is supported by gas-phase studies performed concurrently in our laboratory which show that large amounts of carbon dioxide decrease the signal-to-background ratio for emission from other species (29).

Linearity and Precision. The linearity of emission from the surfatron MIP has previously been reported to be three decades (23). Our studies have

revealed linearity over at least two orders of magnitude for a series of injections ranging from 0.6 ng to 60 ng of thiophene, with a roll-off noted for an injection of 300 ng. The slope of the log-log plot of the first five concentrations is 1.01 with an intercept of 0.575 and a correlation coefficient of 0.999. The relative standard deviation of the peak heights for thiophene was based on four replicate injections of 50 ppm, 100 ppm, and 500 ppm solutions. The values ranged from 1 to 5%.

CONCLUSIONS

Although the findings presented here must be considered preliminary, the attractiveness of the microwave-induced plasma as a detection method for capillary SFC is clearly apparent. Sensitivity and selectivity for sulfur-containing compounds supersede those obtained with the flame photometric detector (FPD) (13). In effect, the surfatron detector is superior to the FPD since the latter suffers from a non-linear sulfur response (31) and the former is capable of detecting many other elements in addition to sulfur. Attractive opportunities for capillary SFC with this type of detection exist in the area of halogenated non-volatile organic compounds where no other existing separation and measurement methods are effective.

Further improvements in detection limits are expected by reducing the background signal through the use of alternative mobile phases. Nitrous oxide is a readily available and commonly used mobile phase in SFC which offers universal detection possibilities analogous to the FID. The attractiveness of this compound has been demonstrated by gas-phase doping of a He plasma which revealed fewer spectral interferences in the near-IR than did CO₂ with respect to many of the non-metals in which we are interested (29).

Another means of increasing sensitivity may be realized by utilizing more efficient signal-processing. One possibility lies in the use of background correction through wavelength modulation. Refractor-plate-modulation is especially useful when the atomic line of interest is superimposed on a band such as CN, which is the specific case for the principal sulfur lines in the near-IR, and may be in part related to the problem of the sloping background observed during a pressure gradient. This area is currently being investigated in our laboratory.

CREDIT

This research was supported by the National Science Foundation through Grants CHE 83-20053 and CHE 86-05935, the Office of Naval Research, SOHIO, and American Cyanamid.

ACKNOWLEDGMENT

The authors gratefully acknowledge Dr. Mark Selby for his technical assistance and for his contribution to the preparation of schematics which were included in this paper.

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Table I. Detection limits for sulfur at 95% confidence level (S/N = 2)

<u>COMPOUND</u>	<u>FORMULA WEIGHT (g/mol)</u>	<u>DETECTION LIMITS (pg/sec)</u>
Thiophene	84	25
Thianaphthene	134	70
Dibenzothiophene	184	150

FIGURE CAPTIONS

Figure 1. Schematic diagram of the supercritical fluid chromatograph, interface, and microwave-induced plasma detector.

Figure 2. Schematic diagram of the SFC/MIP interface.

Figure 3. (a) The effect of microwave power on sulfur emission intensity at 921.3 nm (injections of thiophene). Helium flow rate, 250 mL/min. Slit width, 100 μ m.
(b) The effect of microwave power on chlorine emission intensity at 912.1 nm (injections of solvent). Helium flow rate, 150 mL/min. Slit width, 100 μ m.

Figure 4. (a) The effect of helium flow rate on sulfur emission intensity from replicate injections of thiophene. Microwave power, 120 W. Slit width, 100 μ m.
(b) The effect of helium flow rate on chlorine emission intensity from replicate injections of solvent. Microwave power, 125 W. Slit width, 100 μ m.

Figure 5. Separation of model mixture. Microwave power, 110 W. Helium flow rate, 120 mL/min. Column temperature, 70 °C. Approximately 60 ng of each component was introduced by a single injection.
1 = thiophene; 2 = thianaphthene; 3 = dibenzothiophene;
4 = 1,2-diphenylene sulfide.

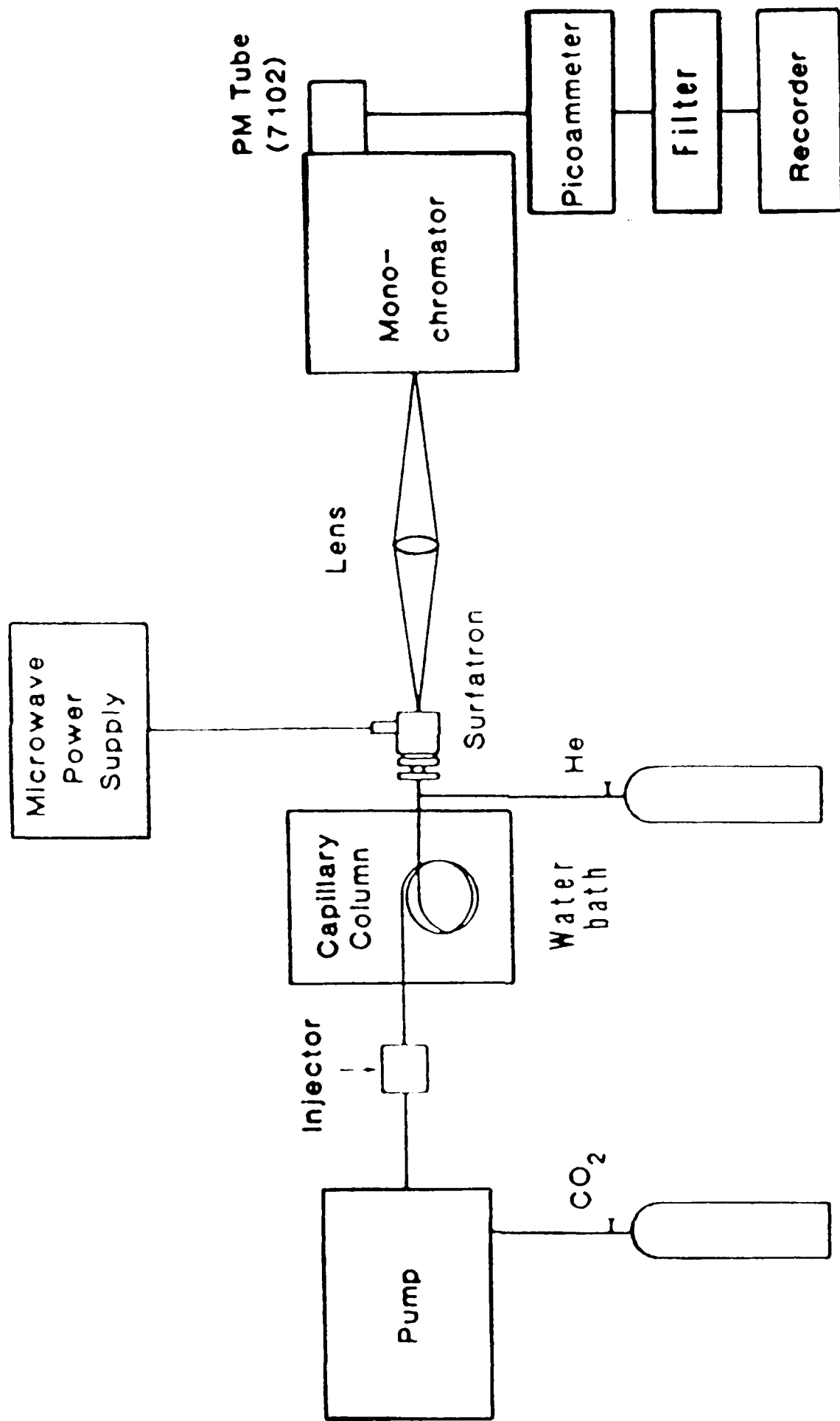


Fig. 1

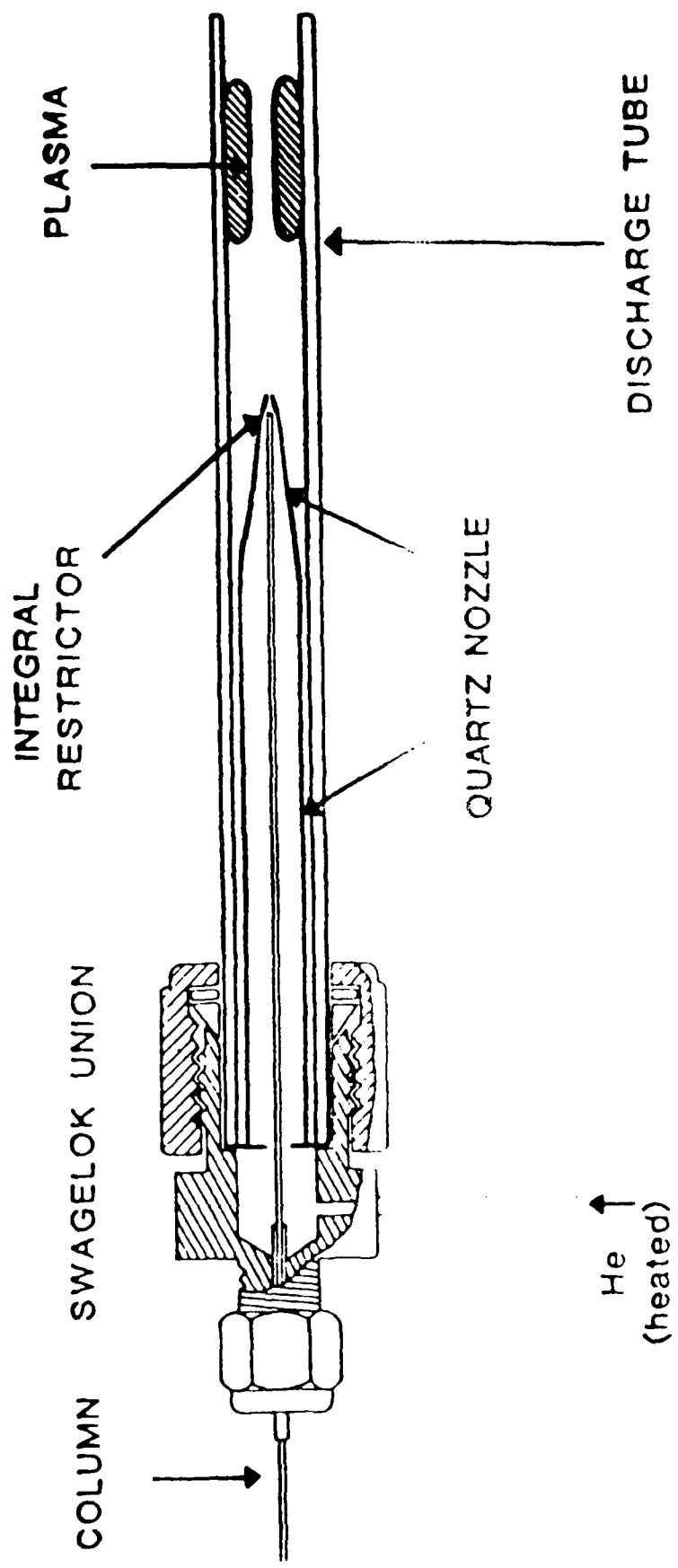


Fig. 2

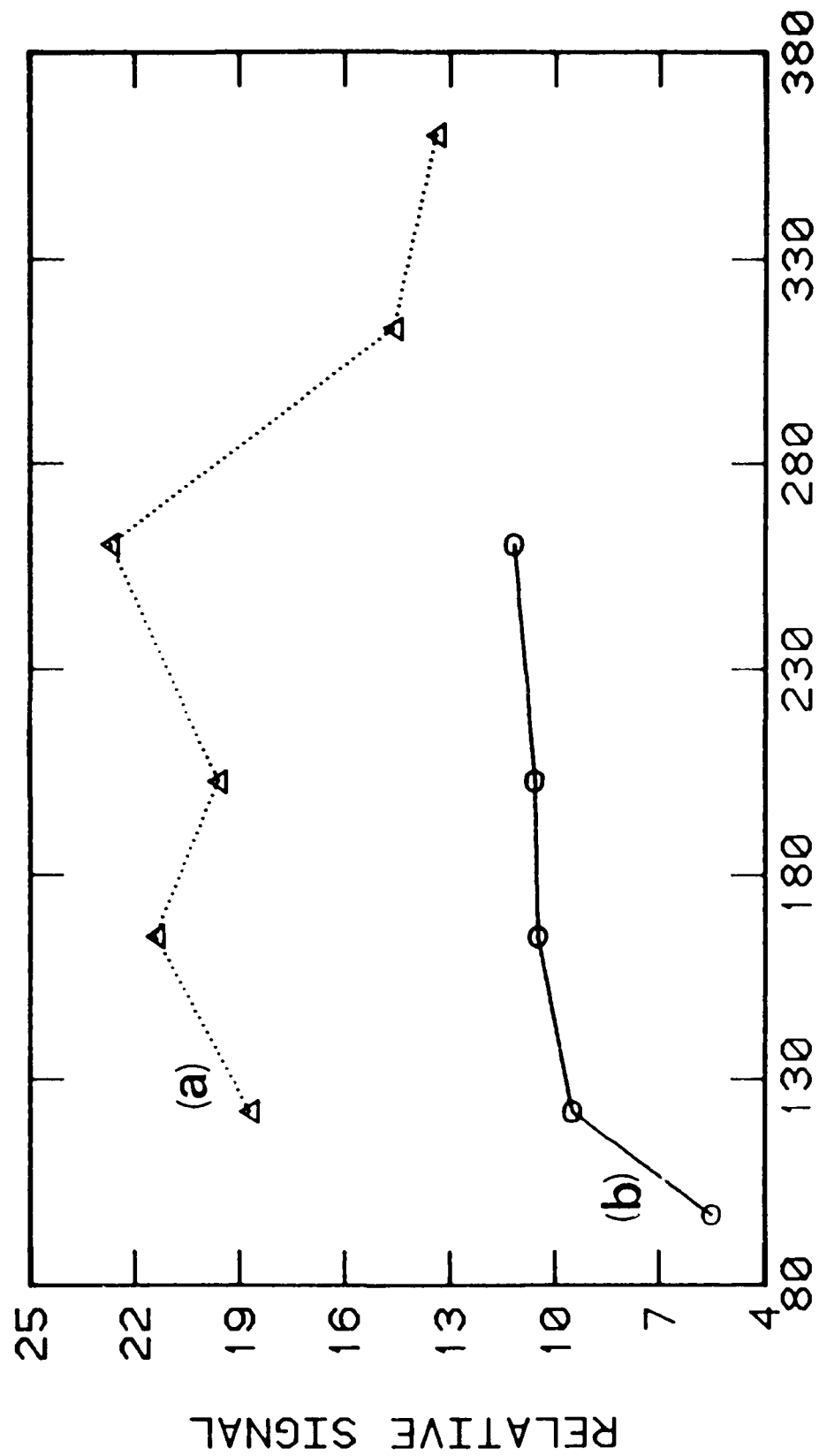


Fig. 3
HELIUM FLOW RATE (mL/min)

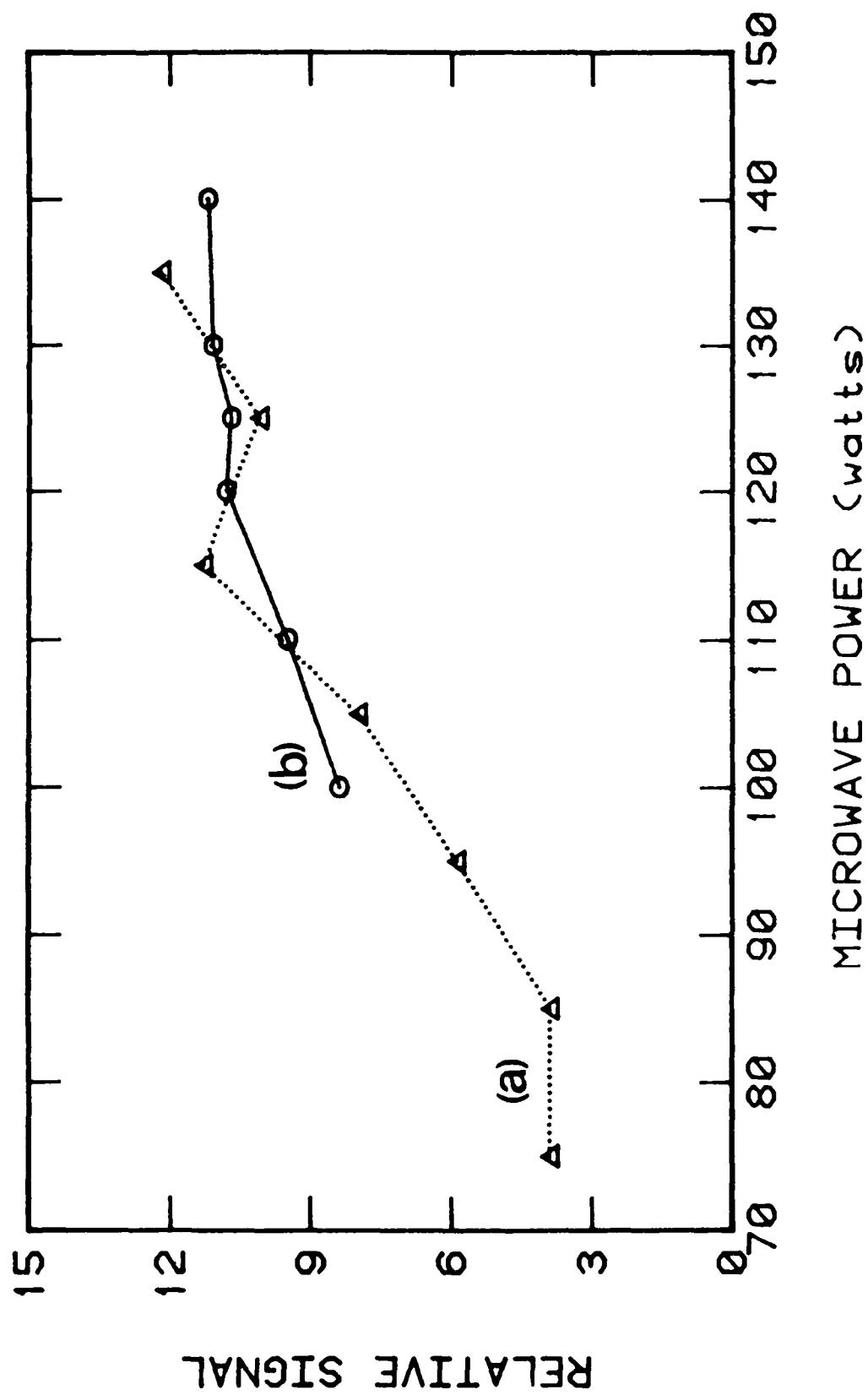
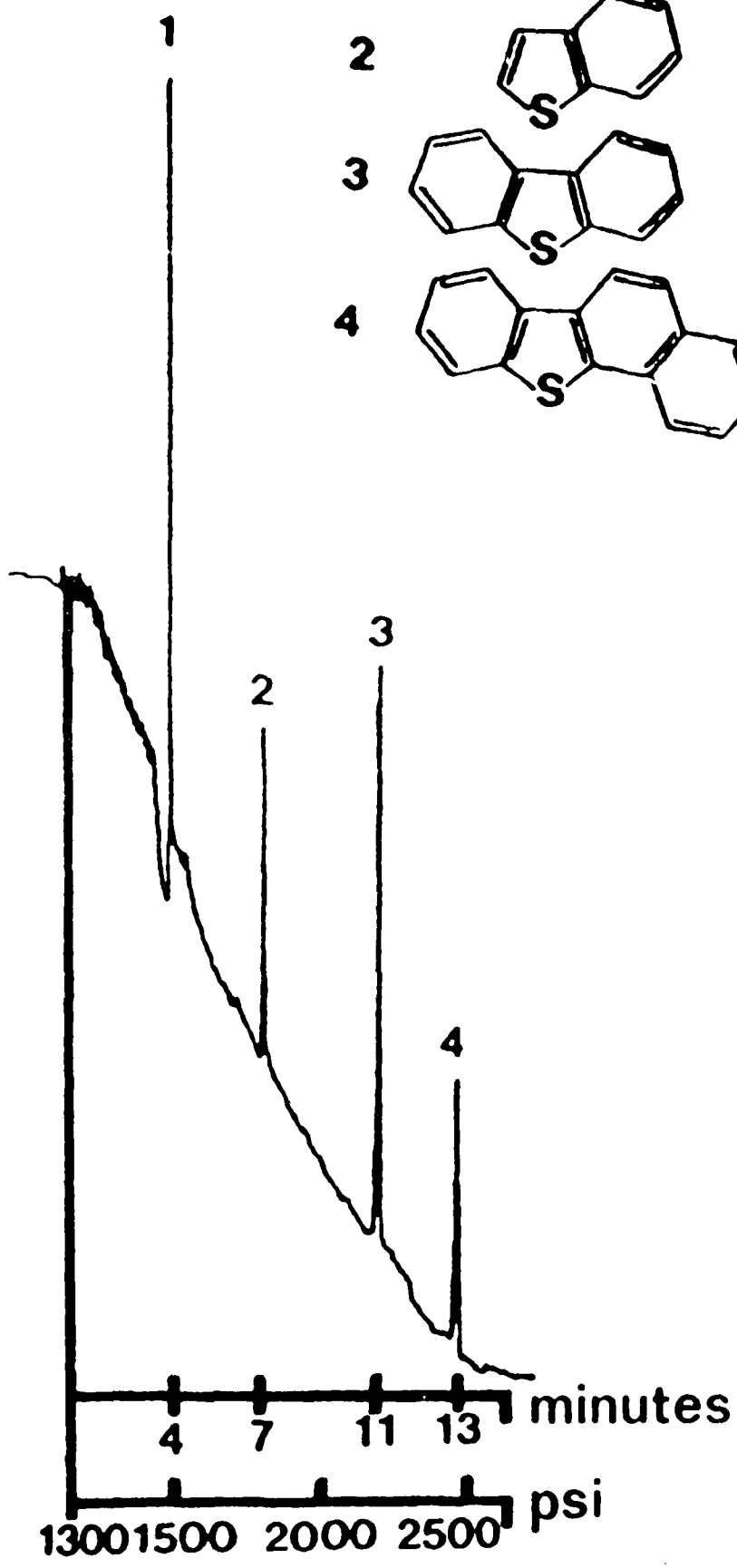
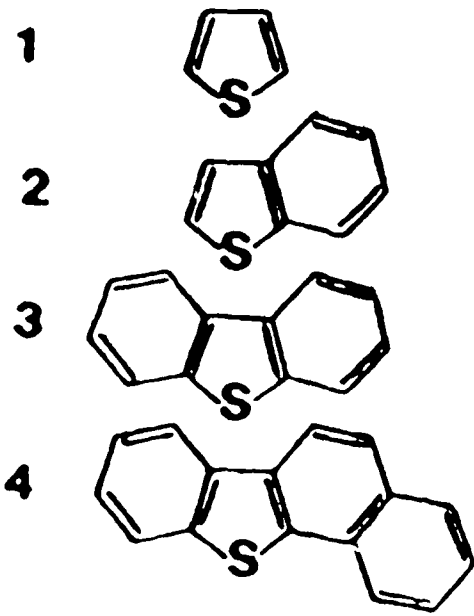


Fig. 4

Fig. 5



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